Methods applied to investigage the major UVCE that occured in the TOTAL refiner's Fluid Catalytic Cracking Unit at La Mède, France

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1. SUMMARY OF THE EVENT

On monday November 9, 1992 at 5:20 a.m. a major U.V.C.E. occured in the Gas Plant of the TOTAL refinery's Fluid Catalytic Cracking Unit at La Mède, France. The origin was a 25 cm^2 break in the 8" by-pass of the absorber stripper column cooler; an amount of about 15 tons of LPG and light naphtha was released within 10 minutes, covering an area of $14000m^2$ including Gas Plant, cryogenic, propene and Merox units before being ignited on the FCC main furnace. There were eight people on shift in the unit: 6 died, one was very seriously injured, and one slightly injured. The total loss including loss of production is estimated at 600,000,000$. (see figure 1)
Direct domino effects resulted from positive and negative overpressures, missiles, and ground shock: fractures of pipework, tank fires and power station fire.
Indirect domino effects were the consequence of fire exposure inducing piping bursting: 5:22 a.m., rupture of the depropanizer head line with consecutive explosion and fireball. (see photograph of figure 2) 5:26 a.m., explosion of the debutanizer head line with fireball. Let us mention also the explosions of a LPG pipeline and a gasoil line. A total of 60 ruptured pipes were observed.

2. METHODOLOGICAL APPROACH

The methodological approach developed by the investigation team comprises 4 main steps:

2.1 Gathering evidence

The search for information involved namely specific data sources:

- control room hard copy and electronically stored records: no deviation of process operating parameters were observed on the 50 measurement records analyzed;
- video tapes from amateurs and newsmedia: 17 films collected covering a period starting at 5h22 a.m. (2 minutes after the first explosion) to 12h00;
- record from a gas detector 3 minutes before the explosion;

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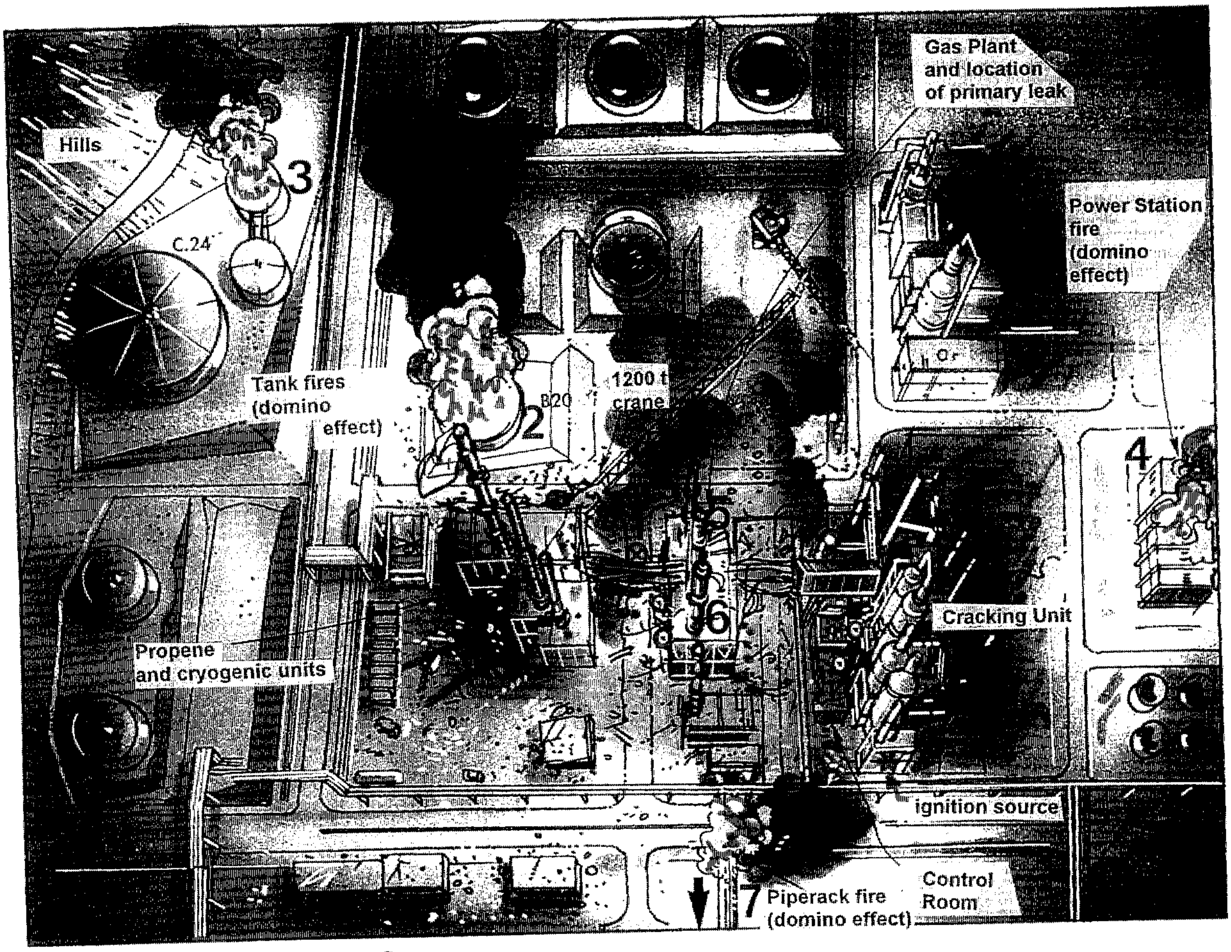

Figure 1. Chronology of Events ⊗ epicentre ⊙ location of victims

Figure 2. 5:22 a.m. second explosion, rupture of the depropanizer head line.

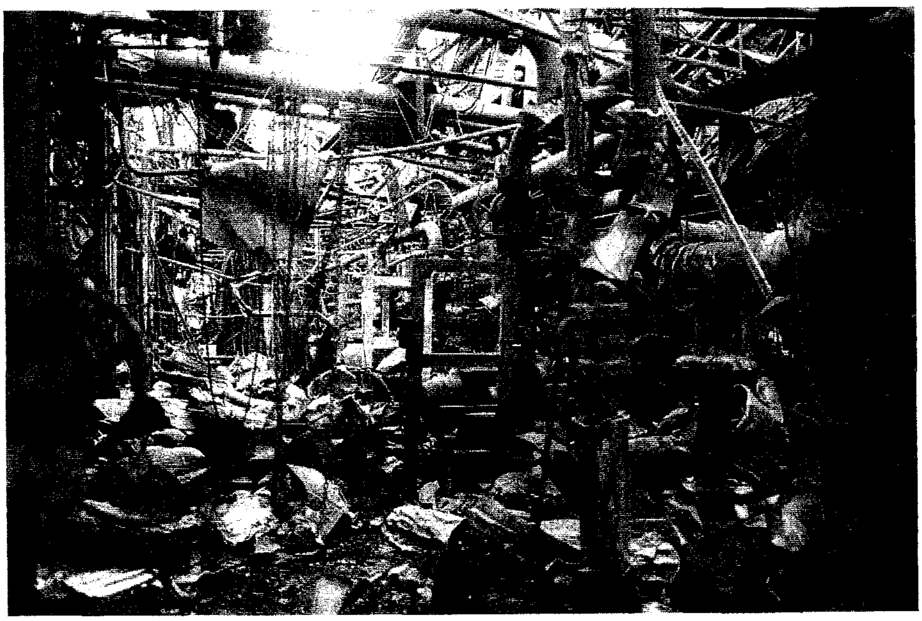

Figure 3. Gas Plant area after explosion and consecutive fires.

- more than 1750 photographs from audit team, professional photographers and amateurs were collected and expertised;
- witnesses interviews;
- missiles mapping;
- seismic waves records collected from 21 stations located between 28 km and 409 km from the epicentre.

2.2 Defining potential scenarios

The selection of the potential accident scenarios was based upon four concepts:

- The determination of the explosive mass and the location of the explosion epicentre extrapolated from the observed damages in both far-field and near-field, using different ways of modeling: multi-energy approach, TNT equivalency and spherical expanding flame model;
- The identification of all potential ignition sources leading to the determination of the one being the origin of the ignition of the vapour cloud: the FCC furnace F301 located at 150m from the epicentre;
- The exhaustive numbering of the ruptured equipment: 60 fractured pipes and branch connections, no capacity nor pressure vessel ruptured;
- The identification of the ruptured pipes that might generate the main explosion, using 3 + 5 criteria.

2.3 Investigating the possible scenario

Finally, 4 systems remained selected for a more complex investigation:

- a soda tank containing accidentally introduced propane,
- the 8" by-pass of the absorber stripper cooler,
- a 1" branch connection (guillotine break) located on the 8" line between cooler and absorber stripper,
- a 3" LPG pipeline.

2.4 Performing the validation of the assumptions

To emphasize the most probable sequence and to perform the validation of the assumptions herewith associated, 5 different tools were used:

- 2D model software for dispersion simulation: gaussian plume model and dense model. The released vapours are heavier than air: (C3, C4 and light naphtha); the refinery is located on ground with slop; at the time of the accident, Pasquill stability class was $F_{0,5}$.
- Wind tunnel simulation with a model of the refinery site on a $1/150^{th}$ scale, using Richardson similarity.
- Dynamic process modeling of the absorber stripper column for determining the time associated with process operating parameters deviation.
- Simulation in a similar unit in another TOTAL refinery.
- Use of metallurgical and mechanical data to confirm the determination of the primary leak.

3. INVESTIGATION INTO THE AMOUNT OF FLAMMABLE PRODUCTS INVOLVED

Inspection of the accident site is one of the most important steps in gathering physical evidence. A detailed examination is made to obtain information on the apparent origin, the propagation of the explosion and localized damage of the explosion or fire. In the case of explosion damage analyses, the main goal is the evaluation of the amount involved, because hereafter it is a very important criterion to classify possible scenarios. Explosion damage is due to the high and dynamic pressures generated by the sudden release of energy. However, the damage analyses include consideration of the following important items:

1. flammable vapour cloud confinement in the installation
2. explosion pressures, propagation rates and energy release
3. near-field effects
4. blast wave or far-field effects.

All these aspects were kept in mind during the damage investigation. A damage table was set up (see table 1). The evaluation of the pressure in the far-field was made by comparison with tabulated blast wave criteria.
Related to the near-field, some mechanical calculations were performed. A map of the fire damage was established too.

Table 1
Some damages observed

Observation point	Effects	Incident pressure (kPa)	Distance (m)
Cryogenic unit	mechanical ruptures	50-100	epicentre area
Propene unit	mechanical ruptures and projectile	50-100	epicentre area
Gantry pipe and pipelines	over balancing	40-55	epicentre area
Gas plant	bending of a column	40-70 70	20
Electrical Station 42	all walls breaking down	40-80	35
Electrical Station 40	all walls arched	30-50	50
Locker room	breaking down	30-50	50
Control room	large eardrum rupture	40-90 50	80
Tanks A38, C24, C25, B14, B56	deformation and displacement	15-25	150-170
Technical building	inside, structural damages and glass windows projection	8-12	200
Neighbouring habitations	glass windows breakage	5-7	700
La Mède	about 50% glass windows breakage	2-3	1000-1400
Commercial Center	large windows breakage	1-2	2100
Martigues, Jonquières and Ferrières	more than 10% of windows breakage	1-2	3500-4500
Martigues, LEP lieu-dit Brise-Lames	several windows breakage	1,5-3	3700
Martigues swimmingpool	several bays windows breakages	1,5-3	3900
Châteauneuf-les-Martigues	bay window breakage	0,5-1,1	4000

One may think that the damages behind the refinery fence, in particular at Martigues, were enhenced due to the meteorological conditions at the time of the explosion. As a first step, the explosion damage analysis allows to determine the epicentre area of the explosion. This area is defined as the location where the pressure was the highest. This epicentre area was located between the propene unit and the Gas Plant. It is different from the ignition point and from the origin of the leak, because the explosion pressure depends strongly on the congested parts on the site. (see photograph of figure 3) As a second step, the examination of the projection of missiles allows to evaluate the pressure at the epicentre area: 50 to 200 kPa locally. Then, several methods were used to determine the amount of flammable mixture involved in the explosion: TNT equivalency, multi-energy method and spherical expanding flame model. For example, the multi-energy method allows to make some comparison between the congested volume from the different units and the damages observed. The objective was to obtain the better curve as possible to reduce the distance between the curve and the damage points (see figure 4). Finally, the different methods led to good agreement about the assessment of the most probable amount of flammable mixture involved in the explosion. The best estimation was about 5 tons scale of sizes.

4. SELECTION OF THE FRACTURED PIPES POSSIBLY IMPLICATED WITH THE PRIMARY LEAK

60 fractures of pipework were observed. In order to identify the ones that might generate the main explosion the following methodological approach based on 3 + 5 criteria was defined. A first selection was made, discarding three families of ruptured pipes:

1. 14 pipes containing products unable to generate an explosion phenomenon such as non flammable products (DEA, water, soda) or flammable products with pressure vapour less than 10hPa at operating temperature (GO, HV fuel, heavy naphtha).
2. 11 pipes being isolated at the time of the explosion and having a small capacity.
3. 12 pipes containing flammable products with specific physical conditions: vapour phase and small pressure (1050hPa).
   For such emission sources we have a mass flow of 2,3 kg/s in vapour phase, an explosive mass of about 2kg and a LEL concentration up to 45m from the source with stability class F1.

For the 23 remaining ruptured pipes, 4 criteria correlated with calculations and one criterion based upon visual inspection are then applied:

1. vapour mass flow must be superior to 10 kg/s;
2. the LEL of the released gaseous mixture must reach the furnace;
3. 20% of the LEL must be snuffed at the location of the gas detector having given an alarm 3 minutes before the explosion happens;
4. the released mass within the explosion limits must be about several tons;

Comparison with observed damages.

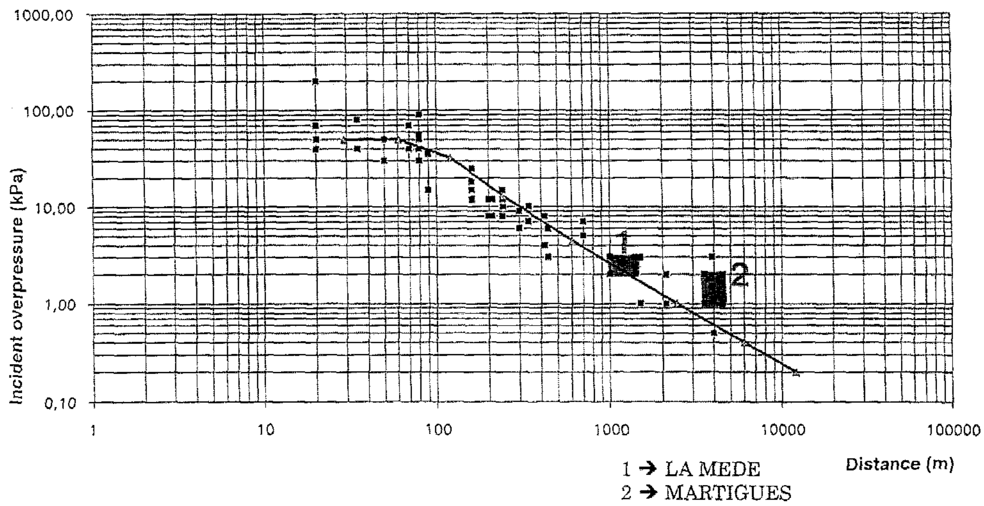

Figure 4. Multi-energy approach: correlation with observed damages corresponding to an hemispherical cloud with a 29m radius.

Figure 5. Ignition source: FCC main furnace.

5. The physical conditions of the rupture are not a consequence of the main explosion.

18 fractured pipes were consequently elaminated by criteria 1 to 4. The five remaining ruptured pipes were then submitted to criteria 5. Three systems then necessitated a more complex analysis:

- 8" by-pass of the absorber stripper cooler;
- 1" branch connection on the 8" line from the absorber stripper cooler;
- 3" butane pipeline T09.

5. ANALYSIS OF POSSIBLE LEAKS

Four likely scenarios were considered. The first is related to a leak on the LPG line T09. When the accident occured, it was isolated and full of liquid butane. It presents a bulge-shaped breach (200x120mm). Owing to the diameter of the line and the pressure inside it, the order of magnitude of the explosive amount of gas would be at the most 80kg, the explosive area extending as far as 45m. Moreover, witnesses saw the line exploding and metallurgical investigation led to plastic deformation due to heating. It was thus possible to discard this hypothesis.

The second scenario is related to C24 tank in which is usually sent the used soda coming from the refining of propane, butane and gasoline. When used soda is drained off, hydrocarbons may be accidentally introduced in the tank. The tank has burnt the day the accident occured. Modeling was performed related to leaks of gas through vents or broader holes, according to the maximum propane release rate that might have been drained to the tank, the maximum explosive mass has been assessed to about 1,2 tons, the maximum extension of the explosive cloud being 100m. The case of leak without kinetic energy has been considered too, by means of a wind-tunnel simulation as described below. It was not possible to guess measurable concentrations in the gas plant. All these reasons led to the discarding of the scenario.

The two last scenarios are related to the absorber stripper DA101, the first about a 1" branch connection and the second about a breach (800x200mm) on the by-pass of the EA103 cooler. More complex simulations including wind tunnel and dynamic process modeling were then used. It was thus possible to emphasize that the most probable origin of the initial leak was the by-pass as shown below.

6. IGNITION SOURCE LOCATION

In an unit, the possible ignition sources may be:

- an electrical spark due to the rupture extra-current of a circuit, generated by some manoeuvre,
- an open flame like a burner of a furnace,
- a mechanical spark,

- hot surfaces the temperature of which being greater than auto-ignition temperature of the flammable products involved.

In our purpose, the investigation dealt with the electric sources and the F301 furnace. In fact, the mechanical spark was not taken into consideration because there was no work in progress, nor abnormal situation in an electrical equipment. The possibility of an ignition on the hot surfaces of the disaster area was not held because the auto-ignition temperature of the gases was greater than the operating temperature of the pipes.

On the other hand, several findings were made under the F301 furnace. The flammable cloud burnt up to the two thirds of the south part of the furnace. Traces of combustion were found on the external box of the third burner at east. More, in the direction of the Gas Plant, several burns, were found on the electrical cabinets and cables indicating the travel of a slow flame front. Several investigations on the electrical equipment were made in order to justify the exclusion of this kind of equipment.

Finally, the ignition on the F301 furnace was found to be the only solution that is consistent with evidence and with the observed traces of combustion. (see photograph of figure 5).

7. VALIDATION OF THE ASSUMPTIONS

7.1 Wind tunnel simulation of the dispersion of the explosive vapour cloud.

The choice of a physical model simulation was dictated by the difficulty of reproducing the complexity of flow phenomena on a site such as La Mède, due to the lack of available accurate models. The experiments were conducted in the diffusion wind tunnel of EDF's Lyon Engineering Center located in the premises of the Fluid Mechanics and Acoustics Laboratory URA CNRS 263 of the "Ecole Centrale de Lyon". This wind tunnel is of the feedback type with venting downstream of the test facility. The test section measures 14 meters in length, 3.70 meters in width and the height is variable between 2 and 2.50 meters. The speed inside the test section is continuously adjustable from 0-10m/s. The model of the La Mède refinery site on a 1/150th scale, represents the whole of the zone affected by the explosion and incorporates the potential release points to be investigated (see photograph of figure 6). The ground incline is perfectly reproduced on the model. The physical model study of the dispersion of an explosive gas cloud heavier than air is performed in Richardson similarity the only scale parameter of which is represented by the Richardson number

$$Ri = g\frac{\rho g - \rho a}{\rho a}\frac{L}{U^2}$$

where g is gravitational acceleration,

$$g' = g\frac{\rho g - \rho a}{\rho a}$$

g' is the gravity term, ρ_g and ρ_a, L and U are respectively the specific masses of gas and air, the characteristic length, and speed scales defined in the case of a continuous gas release at the break of volume flowrate Qv via

$$L = \left(\frac{Q_v^2}{g}\right)^{\frac{1}{5}} \text{ and } U = (Qv\, g')^{\frac{1}{5}}.$$

This definition of the Richardson number, used by Köning-Langlo and Schatzmann (1990) is routinely used for continuous releases in a calm atmosphere, characterized by wing speeds under 1 m/s. A different definition is used for non-zero wind velocities, where the local flow velocity is used to determine the characteristic scales (Britter and McQuaid 1988). Validation tests, presented in particular by Köning-Langlo et al (1990) Hall et al (1982) and Y. Riou (1987), have shown good agreement of the wind tunnel results with those obtained in situ, mainly at Thorney Island (MC Quaid 1984), Porton (Picknett 1978, 1981) for instantaneous gas releases and at Burro (Koopmann et al 1982), Maplin Sands (Puttock) et al 1982) and Thorney Island for continuous gas releases. Instantaneous concentrations are measured by means of a hydrocarbide analyzer (Cambustion Ltd) the passband of which is about 500 Hz for a 150 mm sampling probe lenght. The tracer gases used in the wind tunnel are mainly hydrocarbides whose densities are close to the considered release conditions. The main test results for the three scenarios under consideration have shown, despite the very conservative hypotheses adopted for this simulation, that the maximum gas leak from storage tank C24 could not be the cause of the accident, since the concentration levels reached at the ignition point are far lower than the gas inflammability limit (LEL). Regarding the two absorber stripper cooler EA 103 scenarios, the tests showed that scenario break at the by-pass bounds the second one (failure of 1" branch connection). The gas concentrations at the ignition point (furnace F 301) only reach the LEL for the first scenario. The simulation made for this scenario by east wind led to the results closest to the evidence. Note in particular that the gas cloud reaches both the gas detector P80-1 and the ignition source. The dispersion and transport of the gas cloud particularly made it possible first, to characterize the progression of the explosive mixture as far as the presumed ignition source and, secondly, to evaluate the average time to reach the ignition point by the LEL at 675 ± 110 seconds for 98 simulations, compatible with the estimations made elsewhere (see figure 7).

7.2 Dynamic process modeling of the absorber stripper

If one of the breaks is the origin of the accident, it must be demonstrated that, during the estimated release duration about 10 minutes,

1. the break can release a sufficient mass of product
2. the break is not inducing variations of the operating parameters, as oberved on the hard copy stored records.

To verify both criteria a realistic dynamic process modeling of the absorber stripper column has been performed by the IFP (Institut Français du Pétrole) in order to determine the time associated with process operating parameters

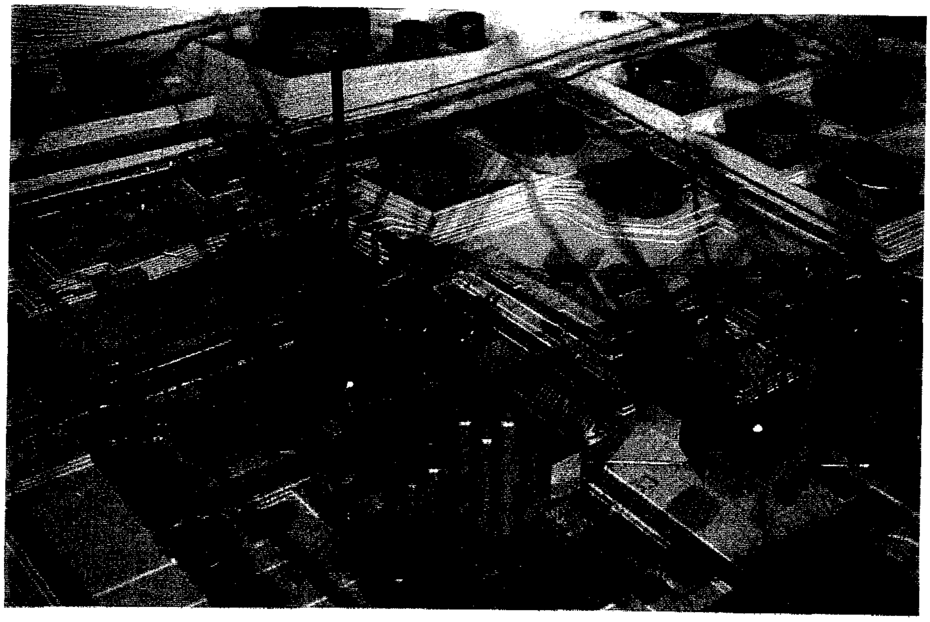

Figure 6. Wind tunnel simulation: 1/150th scale model of the zone affected by the explosion.

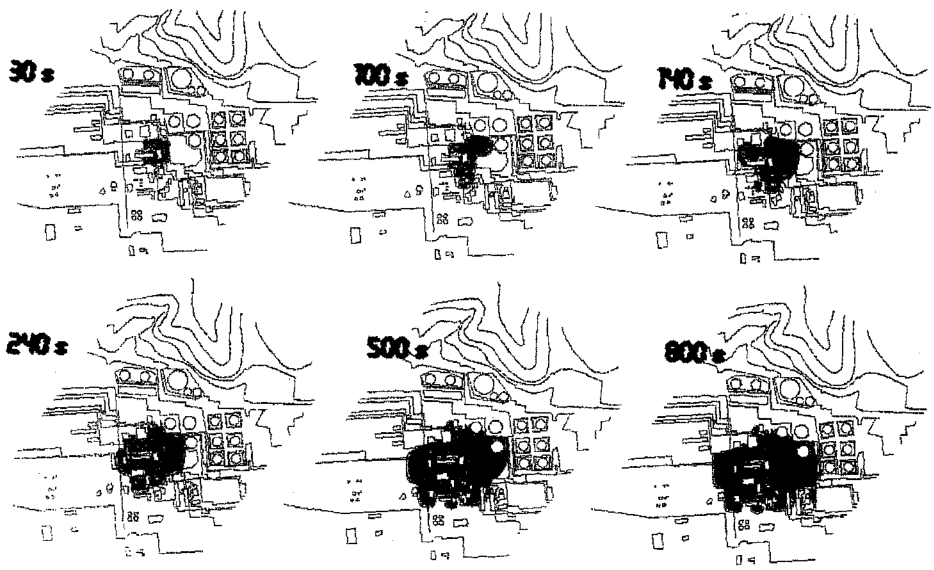

Figure 7. Wind tunnel simulation: dispersion and transport of the vapour cloud (8" by-pass case) as a function of time.

deviations. This evaluation technique combines physical models for quantifying release outflow with transfer functions calibrated by mean of test done on a similar column in another TOTAL refinery. From that dynamic simulation it has been demonstrated that for outflow opening areas less than $35cm^2$, pressure variations are not detectable before a 30 minutes period; for hole areas less or equal to $25cm^2$, no noticeable variations is observed for the absorber bottom level, for the head vapour flow and for the bottom liquid flow, if the release lasts less than 10 minutes. Taking into account the operating process conditions at the time of the accident, this dynamic process simulation has shown that within 10 minutes:

1. 12 tons of hydrocarbons might have been released through a $25cm^2$ break area, the third part of this amount being vaporized.
2. Through the 1" branch connection 5 tons might have been released, thus discarding this branch connection scenario.

8. CONCLUSIONS

From the experience gained at La Mède, it was possible to point out the following recommendations to perform an accident investigation:

1. It is required for companies to develop incident investigation system involving top management.
   The Chairman of the investigation team has to be a manager experienced in operating production units, to know technology and process of the implicated kind of unit and, finally, has to be aware of safety aspects.
2. An investigation team has to be constituted with internal and external multi-disciplinary experts (fluid mechanics, detonics, mechanics, electricity, metallurgy, industrial risk analysis, process control...).
3. It is necessary to visit the site as soon as possible to identify and secure area of interest and photograph the maximum of exhibits.
4. It is recommended to associate operators and maintenance crew to the investigation, particularly when gathering evidences and trying to demonstrate the feasibility of scenarios.
5. Validation of the assumptions must be performed by using different modeling and simulation approaches in order to point out the most probable root cause event.
6. In order to increase the knowledge in learning from accidents, it would be useful to collect as precisely as possible and disseminate all the relevant information: lectures, papers, investigation report with non restricted distribution... .